29. Effect of Non-planarity on the Spin Distribution in the Radical Anions Containing the Stilbene or the Azobenzene π-System: An ESR and ENDOR Study

by **Fabian Gerson***, **Axel Lamprecht**, **Markus Scholz**, and **Heinz Troxler**

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and **Dieter Lenoir**

Institut für Ökologische Chemie, GSF Forschungszentrum für Umwelt und Gesundheit, Postfach 1129, D-85758 Oberschleissheim

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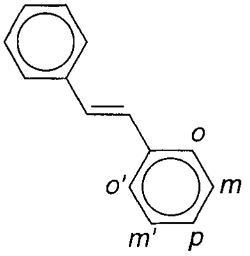
The radical anions of 5*H*-dibenzo[*a,d*]cycloheptene (**9**), 5*H*-dibenzo[*c,f*][1,2]diazepine (**10**), 5,6-dihydrodibenzo[*a,e*]cyclooctene (**11**), 5,6-dihydrodibenzo[*c,g*][1,2]diazocine (**12**), and (*E*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene (**13**) were characterized by ESR and ENDOR spectroscopy. Their hyperfine data were compared with those previously reported for radical anions also containing the stilbene or the azobenzene π-system. Whereas the π-spin distribution in the radical anions of the stilbene series is only moderately sensitive to deviations of the π-system from planarity, the radical anions of the azobenzene series respond to steric strain by shifting the π-spin population from the benzene rings to the azo group. This finding is impressively demonstrated by the similar hyperfine data for $\mathbf{9}^{\cdot-}$ and $\mathbf{11}^{\cdot-}$ which contrast with the strongly differing ones for their azo counterparts $\mathbf{10}^{\cdot-}$ and $\mathbf{12}^{\cdot-}$, as well as by the corresponding values for sterically highly hindered $\mathbf{13}^{\cdot-}$. A plausible interpretation is readily provided by the electron affinities of the constituent π-moieties in stilbene and azobenzene. While those of benzene and ethene are both comparatively low, the azo group has a considerably higher electron affinity.

Introduction. – The isoelectronic (*E*)-stilbene (**1**) and (*E*)-azobenzene (**2**) belong to the basic organic compounds of which radical anions were first investigated by ESR spectroscopy 30 years ago [1–3], and which have since been repeatedly studied by ESR and ENDOR techniques [4–6]. Due to the pronounced electron affinity of the azo group, the half-wave potential of **2** (−1.38 V *vs.* SCE [6]) is markedly less negative than that of **1** (−2.22 V [7]). Despite this difference, the radical anions $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ have a similar π-spin distribution which is evidently governed by the same topology of their π-systems. It may, however, be argued that this distribution will be affected differently by deviations of the π-system from planarity.

Conversion of **1** and **2** into their corresponding (*Z*)-isomers **3** and **4** is a straightforward way to increase such deviations. Both radical anions, $\mathbf{3}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$, are not persistent because they rapidly isomerize to $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$, respectively. Nevertheless, $\mathbf{3}^{\cdot-}$ could be characterized by the hyperfine data under specific conditions [8], whereas its azo counterpart $\mathbf{4}^{\cdot-}$ has hitherto escaped detection by ESR spectroscopy [9]. Besides $\mathbf{3}^{\cdot-}$, the radical anions of the four 1,2-diphenylcycloalkenes **5**–**8** were studied by ESR and ENDOR techniques. In these compounds, where the alkene is propene ($n = 1$) [10], butene ($n = 2$) [11] [12], pentene ($n = 3$) [12], or hexene ($n = 4$) [13], the (*Z*)-configuration of **3** is fixed by incorporation of the central C=C bond into the cycloalkene ring. For obvious reasons, an analogous insertion of the azo group of **4** into a ring is not practicable. On the other hand, the (*Z*)-configuration of both **3** and **4** can be fixed by a CH_2 or a CH_2CH_2 group linking *ortho*-positions of the Ph substituents. Such a bridging yields 5*H*-dibenzo[*a,d*]cyclo-



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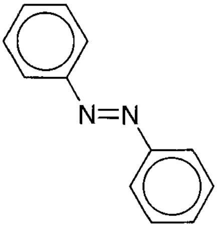

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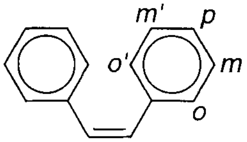

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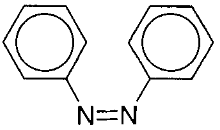

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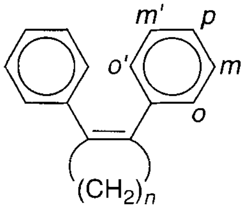
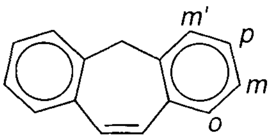


5 $n = 1$
6 $n = 2$
7 $n = 3$
8 $n = 4$



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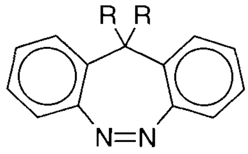

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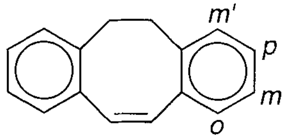
D_2-**10** R = D



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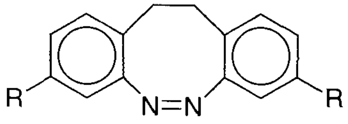
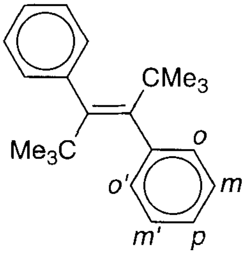


12 R = H
D_2-**12** R = D



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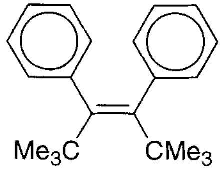

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heptene (**9**) and 5,6-dihydrodibenzo[*a,e*]cyclooctene (**11**) in the series of stilbene and 5*H*-dibenzo[*c,f*][1,2]diazepine (**10**) and 5,6-dihydrodibenzo[*c,g*][1,2]diazocine (**12**) in that of azobenzene.

In the present work, we reinvestigated $\mathbf{9}^{\cdot-}$ [8] [14] with the use of ESR, ENDOR, and general-TRIPLE-resonance spectroscopy and applied these techniques to $\mathbf{10}^{\cdot-}$–$\mathbf{12}^{\cdot-}$. Our studies also include the radical anion obtained from (*E*)- and (*Z*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-enes (= 1,1′-[1,2-bis(1,1-dimethylethyl)ethene-1,2-diyl]bis(benzenes);

13 and **14**), in which the bulky *tert*-butyl substituents at the central C=C bond of **1** and **3** force the Ph groups into positions almost perpendicular to this bond. The results for **9**$^{\cdot-}$–**14**$^{\cdot-}$ are compared with the corresponding data for **1**$^{\cdot-}$–**3**$^{\cdot-}$ and **5**$^{\cdot-}$–**8**$^{\cdot-}$ and discussed in the light of the deviations of the stilbene or azobenzene π-systems from planarity.

Results. – *5*H*-Dibenzo[*a,d*]cycloheptene* (**9**), *5*H*-Dibenzo[*c,f*][1,2]diazepine* (**10**), *5,6-Dihydrodibenzo[*a,e*]cyclooctene* (**11**), *and 5,6-Dihydrodibenzo[*c,g*][1,2]diazocine* (**12**). The radical anions **9**$^{\cdot-}$–**12**$^{\cdot-}$ were generated from their neutral precursors with K in 1,2-dimethoxyethane (DME). Their ESR spectra markedly depended on the temperature, due to conformational mobility of the CH_2 or CH_2CH_2 bridging groups. As we are here concerned with the spin distribution within the stilbene or the azobenzene π-system, the reported results were confined to the temperature range of 193–213 K, in which the conformations of these groups are frozen on the hyperfine time-scale. In contrast to the well-resolved ESR spectra of the hydrocarbon radical anions **9**$^{\cdot-}$ and **11**$^{\cdot-}$, those of their azo counterparts **10**$^{\cdot-}$ and **12**$^{\cdot-}$ suffer from line broadening by a pronounced ^{14}N-hyperfine anisotropy which particularly affects the outer components ($M_I(^{14}\mathrm{N}) \neq 0$). Thus, while the ENDOR technique was very helpful but not indispensable for the analysis of the ESR spectra of **9**$^{\cdot-}$ and **11**$^{\cdot-}$, it proved crucial for unravelling the incompletely resolved hyperfine patterns of **10**$^{\cdot-}$ and **12**$^{\cdot-}$, as illustrated in *Figs. 1* and *2*. For **10**$^{\cdot-}$, not only the coupling constants of the protons (a_H) but also those of the ^{14}N nuclei (a_N) could be determined from the positions of the pertinent ENDOR signals, albeit at somewhat higher temperature than that applied to the protons. On passing to D_2-**10**$^{\cdot-}$, in which the CH_2 bridging group was deuterated, one of the three protons giving rise to $|a_\mathrm{H}| = 0.132$ mT and the single proton having $|a_\mathrm{H}| = 0.025$ mT were substituted by deuterons. In D_2-**12**$^{\cdot-}$, deuterated in the *meta*-positions *m* (*i.e.*, *para* to the CH_2CH_2 bridging group), the two deuterons replaced protons with $|a_\mathrm{H}| = 0.063$ mT. The ESR spectra of both **10**$^{\cdot-}$ and **12**$^{\cdot-}$ and their deuterio derivatives exhibited resolved splittings through coupling (a_K) with the ^{39}K nucleus of the counterion.

*(*E*)- and (*Z*)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-enes* (**13** and **14**). Reduction of **13** and **14** with K in DME led directly to diamagnetic dianions, solutions of which remained ESR-silent unless subjected to UV irradiation by a Hg/Xe lamp. The radical anions then formed from the dianions by loss of an electron reverted to the doubly charged species within 5–10 min after the UV irradiation was turned off.

$$\mathbf{13}(\mathbf{14}) \xrightarrow{+2e^-} \mathbf{13}^{2-}(\mathbf{14}^{2-}) \underset{\text{dark, }+e^-}{\overset{h\nu,-e^-}{\rightleftarrows}} \mathbf{13}^{\cdot-}(\mathbf{14}^{\cdot-})$$

Formation and decay of the radical anions were indicated by the emergence and disappearance of ESR signals. Starting from either isomer, **13** or **14**, the *same* ESR spectrum, shown in *Fig. 3*, was observed. Its hyperfine pattern is somewhat blurred by an underlying S-shaped absorption which presumably arises from an electron exchange between the radical anion and the dianion present in large concentration. Therefore, as in the case of **10**$^{\cdot-}$ and **12**$^{\cdot-}$, the ENDOR technique was required for a reliable analysis of the ESR hyperfine pattern. Because of the short life-time of the radical anion in the absence of irradiation, the ENDOR spectrum had to be recorded by an accumulation of signals obtained immediately after each period of exposure to the Hg/Xe lamp[1]). This spectrum (*Fig. 3*)

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[1]) Our equipment does not allow the use of the ENDOR technique while the sample is being irradiated.

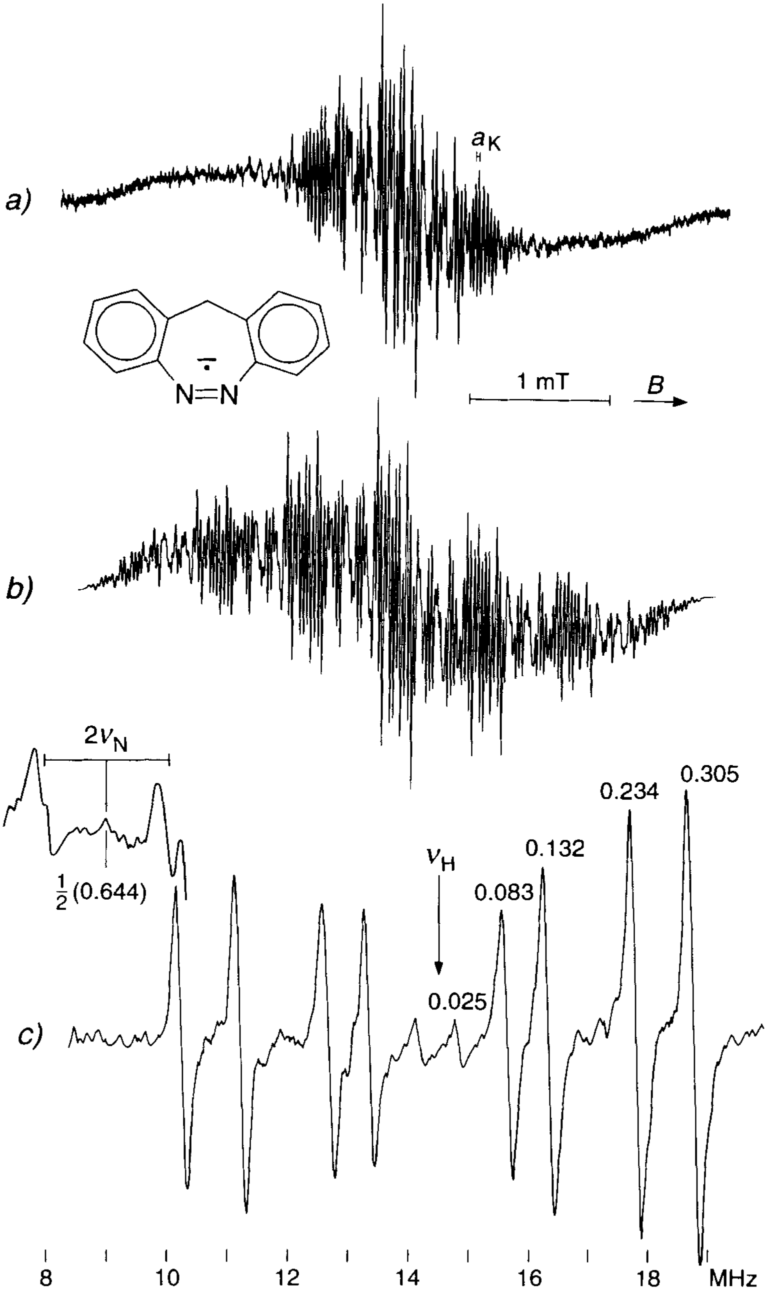

Fig. 1. a) *ESR Spectrum of* **10**$^{\cdot-}$ (solvent DME, counterion K$^+$, temp. 203 K); b) *simulation with the use of the coupling constants* a_H *and* a_N *in* Table 2 (line-shape *Lorentz*ian, line-width 0.03 mT; the effect of ^{14}N anisotropy is not accounted for); c) *^{1}H-ENDOR spectrum of* **10**$^{\cdot-}$ (taken under the same conditions) *and ^{14}N-ENDOR signals* (inset top, left; observed at 263 K). The numbers above the proton signals and below the ^{14}N signals are the $|a_H|$ and $|a_N|$ values in mT.

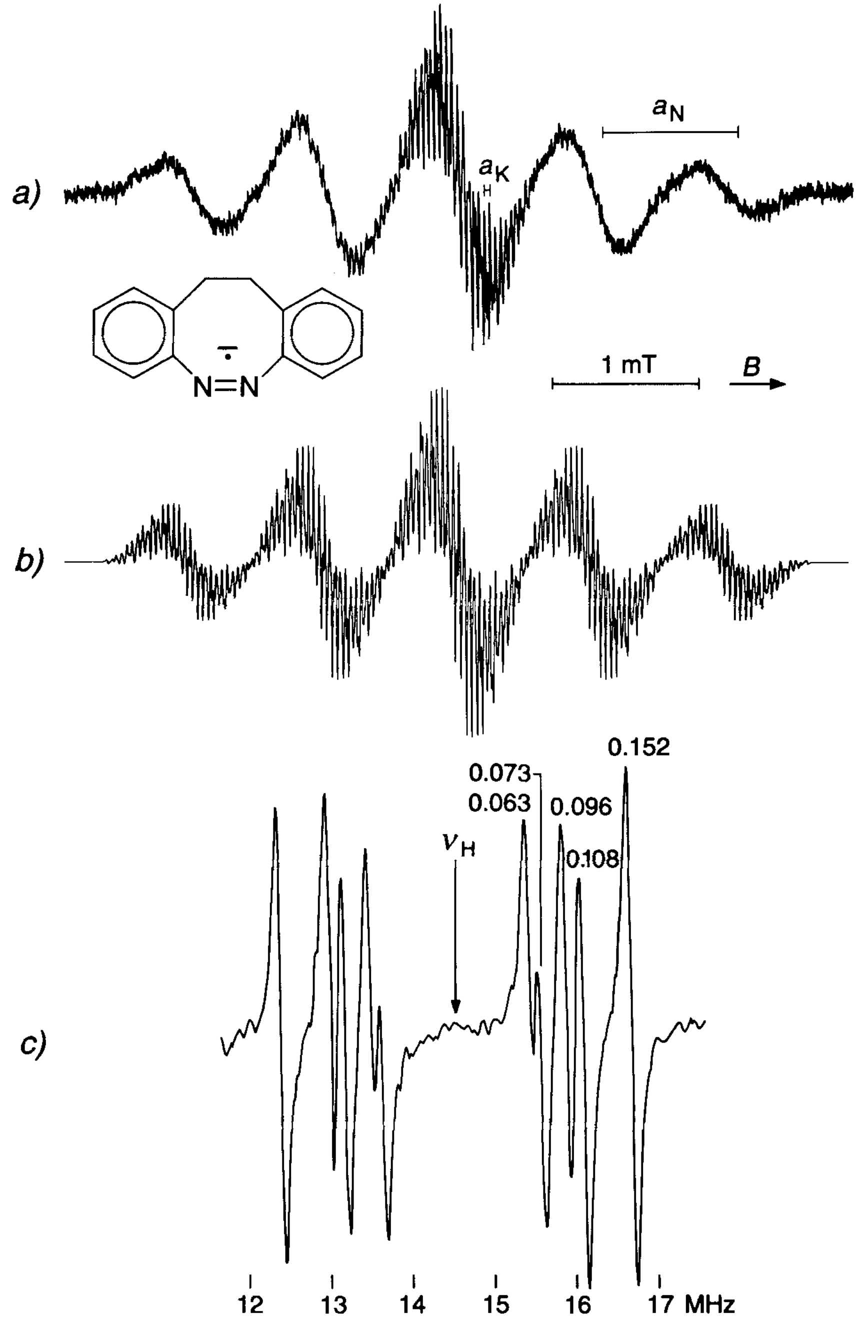

Fig. 2. a) *ESR Spectrum of* **12**$^{\cdot-}$ (solvent DME, counterion K^+, temp. 203 K); b) *simulation with the use of the coupling constants* a_H *and* a_N *in* Table 2 (line-shape *Lorentz*ian, line-width 0.02 mT; the effect of ^{14}N anisotropy is not accounted for); c) *^{1}H-ENDOR spectrum of* **12**$^{\cdot-}$ (taken under the same conditions). The numbers above the signals are the $|a_H|$ values in mT.

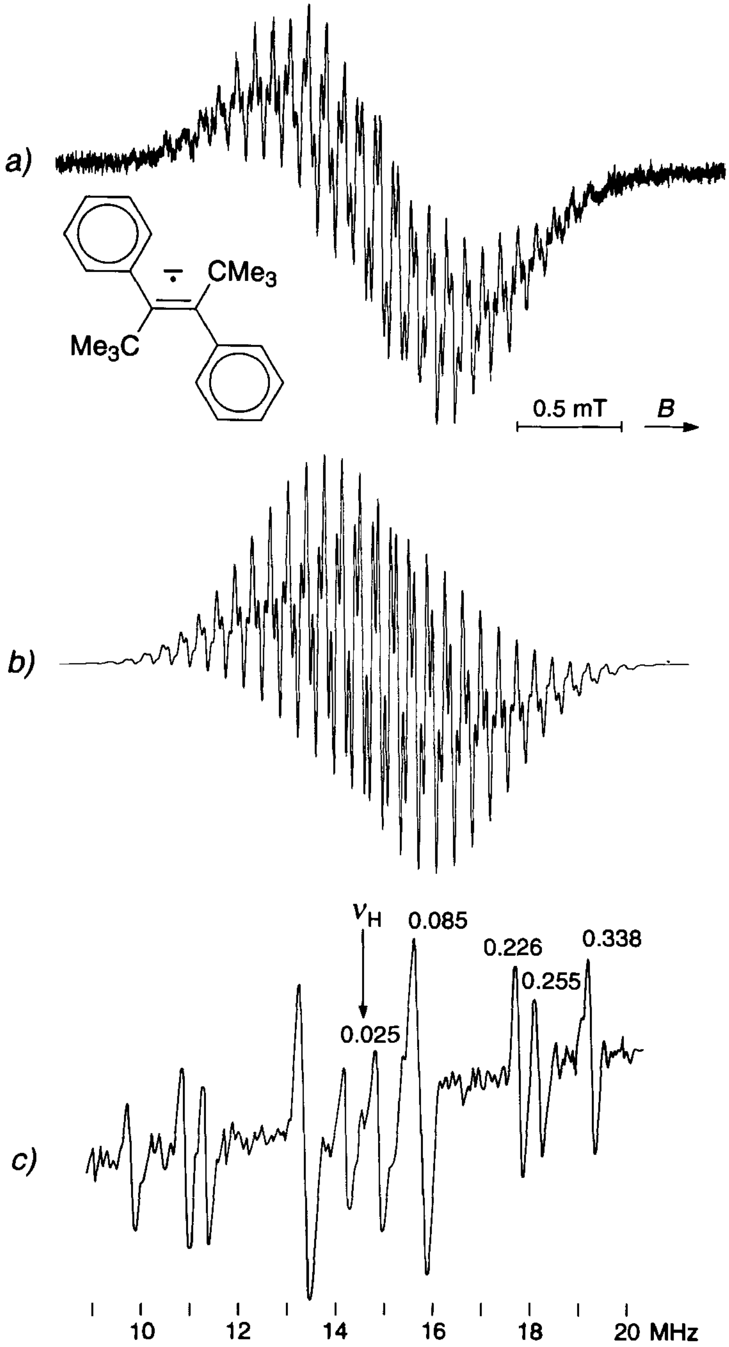

Fig. 3. a) *ESR Spectrum of* **13**$^{\cdot-}$ (solvent DME, counterion K^{+}, temp. 203 K); b) *simulation with the use of the coupling constants* a_H *in* Table 1 (line-shape *Lorentz*ian, line-width 0.04 mT); c) *^{1}H-ENDOR spectrum of* **13**$^{\cdot-}$ (taken under the same conditions). The numbers above the signals are the $|a_H|$ values in mT.

was also independent of the starting material, **13** or **14**. The finding that the same radical anion is formed from either isomer may be rationalized in terms of a (*Z*) → (*E*) conversion, analogous to that following the reduction of **3** and **4**. The observed spectra are thus tentatively attributed to the radical anion $\mathbf{13}^{\cdot-}$ with an (*E*)-like configuration, whereby the (*Z*) → (*E*) isomerization probably occurs *via* the dianion stage (see *Discussion*), as in the case of **3** [8] and **4** [9].

The *g* factors of the hydrocarbon radical anions, $\mathbf{9}^{\cdot-}$, $\mathbf{11}^{\cdot-}$, and $\mathbf{13}^{\cdot-}$, are 2.0027 ± 0.0001, while those of the species containing the azo group, $\mathbf{10}^{\cdot-}$ and $\mathbf{12}^{\cdot-}$, come to 2.0037 ± 0.0002.

Assignments of the Coupling Constants. Tables 1 and *2* list the hyperfine data for $\mathbf{9}^{\cdot-}$–$\mathbf{13}^{\cdot-}$, along with the corresponding values taken from the literature for $\mathbf{1}^{\cdot-}$ [8], $\mathbf{2}^{\cdot-}$ [6], $\mathbf{3}^{\cdot-}$ [8], $\mathbf{5}^{\cdot-}$ [10], $\mathbf{6}^{\cdot-}$ [12], $\mathbf{7}^{\cdot-}$ [12], and $\mathbf{8}^{\cdot-}$ [13]. The signs of the coupling constants a_H agree with the evidence from general-TRIPLE-resonance spectra [15] and with the requirements of experience and theory. Accordingly, the a_H values of the α-protons[2]) at the central C=C bond and in the *para*- and *ortho*-positions of the benzene moieties should be negative, whereas positive values are indicated for such protons in the *meta*-positions [13]. A positive sign is also required for the coupling constants of β-protons[2]) in $\mathbf{5}^{\cdot-}$–$\mathbf{12}^{\cdot-}$ and the ^{14}N nuclei (a_N) in $\mathbf{2}^{\cdot-}$, $\mathbf{10}^{\cdot-}$, and $\mathbf{12}^{\cdot-}$; likewise those of the ^{39}K isotopes (a_K) in the K^+ counterions of $\mathbf{2}^{\cdot-}$, $\mathbf{10}^{\cdot-}$, and $\mathbf{12}^{\cdot-}$ are presumably positive [16]. Assignments of the a_H values to protons in individual positions were based on arguments presented below.

For the radical anions of (*E*)-stilbene (**1**) and (*E*)-azobenzene (**2**), the assignments in *Tables 1* and *2* were confirmed by specific deuterations [2] [3] [6] and alkyl substitutions [4–6]. In particular, ESR and ENDOR studies on the radical anions of 2,2′- and 3,3′-di-

Table 1. *^1H-Coupling Constants* a_H [mT]a)) *for the Radical Anions* $\mathbf{1}^{\cdot-}$, $\mathbf{3}^{\cdot-}$, $\mathbf{5}^{\cdot-}$–$\mathbf{9}^{\cdot-}$, $\mathbf{11}^{\cdot-}$, *and* $\mathbf{13}^{\cdot-}$ *Containing the Stilbene π-System.* Solvent DME, counterion K^+, temp. 203 K, unless otherwise indicated.

	α-Protons[2])						β- and γ-Protons[2])
	2 H_o	2 H_m	2 H_p	2 $H_{m'}$	2 $H_{o'}$	CH=CH	
$\mathbf{1}^{\cdot-}$	−0.193	+0.029	−0.398	+0.082	−0.302	−0.449	
$\mathbf{3}^{\cdot-}$	−0.194	+0.030	−0.386	+0.088	−0.291	−0.268	
$\mathbf{5}^{\cdot-}$b))	−0.253	+0.058	−0.458	+0.077	−0.286	–	+0.193(2β)
$\mathbf{6}^{\cdot-}$	−0.229	+0.048	−0.424	+0.074	−0.275	–	+0.431(4β)
$\mathbf{7}^{\cdot-}$	−0.206	+0.036	−0.381	+0.078	−0.263	–	+0.659(2β); +0.293(2β) 0.036(2γ)c))
$\mathbf{8}^{\cdot-}$	−0.208	+0.042	−0.359	+0.082	−0.249	–	+0.992(2β); +0.391(2β) −0.020(2γ); 0.005(2γ)c))
$\mathbf{9}^{\cdot-}$d))	−0.227	+0.052	−0.422	+0.097	–	−0.422	+0.103(1β); +0.013(1β)
$\mathbf{11}^{\cdot-}$	−0.238	+0.059	−0.387	+0.076	–	−0.428	+0.321(2β); < 0.01(2β)
$\mathbf{13}^{\cdot-}$	−0.226	+0.025e))	−0.338	+0.085e))	−0.255	–	+0.085(18γ)f))

a)) Experimental error: ±0.001 and ±0.002 mT for $|a_H|$ smaller and larger, respectively, than 0.1 mT.

b)) Solvent THF, counterion Na^+.

c)) Sign undetermined.

d)) Values in general agreement with those reported in [8] [14].

e)) See *Footnote 3* for this assignment.

f)) Sign not fully secured by experiment; confirmed by DFT calculations [19].

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[2]) In ESR spectroscopy, protons separated from a π-center by 0, 1, 2, … sp^3-hybridized C-atoms are denoted $\alpha, \beta, \gamma, \ldots$.

Table 2. *^{1}H-, ^{14}N-, and ^{39}K-Coupling Constants* a_H, a_N, *and* a_K [mT][a]) *for the Radical Anions* $\mathbf{2}^{\cdot-}$, $\mathbf{10}^{\cdot-}$, *and* $\mathbf{12}^{\cdot-}$ *Containing the Azobenzene π-System*. Solvent DME, counterion K^{+}, temp. 203 K.

	α-Protons[2])					$2\,^{14}$N	β-Protons[2])	^{39}K
	2 H$_o$	2 H$_m$	2 H$_p$	2 H$_{m'}$	2 H$_{o'}$			
$\mathbf{2}^{\cdot-}$	−0.211	+0.062	−0.320	+0.089	−0.294	+0.478	–	< 0.01[b])
$\mathbf{10}^{\cdot-}$	−0.234	+0.083	−0.305	+0.132	–	+0.644	+0.132(1β)[c]); +0.025(1β)[c])	+0.029
$\mathbf{12}^{\cdot-}$	−0.096[d])	+0.063[c])	−0.108[d])	+0.073	–	+0.915	+0.152(2β); < 0.01(2β)	+0.040

[a]) Experimental error: ±0.001 and ±0.002 mT for $|a_H|$ smaller and larger, respectively, than 0.1 mT; ±0.005 for $|a_N|$ and ±0.002 mT for a_K.

[b]) Too small to be resolved at 203 K; +0.041 mT at 298 K [6].

[c]) Assignment confirmed by deuteration.

[d]) A reverse assignment of these values to the *o*- and *p*-positions cannot be excluded.

alkyl derivatives of **1** [5] and **2** [4] [6] allowed one to distinguish between the two pairs of nonequivalent protons in the *ortho*-positions (*o* and *o'*) and, similarly, between two such pairs in the *meta*-positions (*m* and *m'*). The coupling constants of the *ortho*-protons with the larger absolute value ($\mathbf{1}^{\cdot-}$: −0.302 mT; $\mathbf{2}^{\cdot-}$: −0.294 mT) could be unequivocally assigned to the sterically more congested *o'*-positions; likewise, those of the *meta*-protons with the larger $|a_H|$ value ($\mathbf{1}^{\cdot-}$: +0.082 mT; $\mathbf{2}^{\cdot-}$: +0.089 mT) were attributed to the adjacent *m'*-positions. Use was also made of specific deuteration for assignments of some coupling constants a_H to protons in the radical anions of (*Z*)-stilbene (**3**) [8]. However, as the rapid (*Z*)→(*E*) isomerization prevented the observation of the ESR spectrum of the radical anion of 2,2'-dimethyl-(*Z*)-stilbene [9], the two pairs of nonequivalent *ortho*-protons in $\mathbf{3}^{\cdot-}$ could not be distinguished by the same procedure as that applied to $\mathbf{1}^{\cdot-}$. Still, by analogy with $\mathbf{1}^{\cdot-}$, it is reasonable to assign the coupling constants of *ortho*- and *meta*-protons in $\mathbf{3}^{\cdot-}$ with the larger absolute values (−0.291 and +0.088 mT) to the protons in the sterically more congested *o'*-positions and their neighbors *m'*, respectively. Similar arguments served for assignments of the a_H values to Ph protons in corresponding positions of the radical anions of 1,2-diphenylcycloalkenes **5**–**8** containing the (*Z*)-stilbene π-system (*Table 1*).

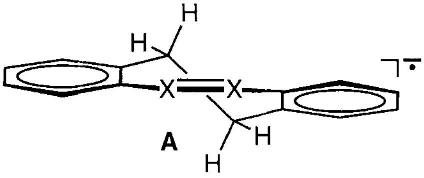
In the radical anions of 5*H*-dibenzo[*a,d*]cycloheptene (**9**), 5,6-dihydrodibenzo[*a,e*]-cyclooctene (**11**), and their aza analogues **10** and **12**, the protons in the congested *o'*-positions of (*Z*)-stilbene or (*Z*)-azobenzene are eliminated by CH_2 or CH_2CH_2 bridging groups. Assignments of the coupling constants a_H to the protons in the remaining positions are consistent with those for $\mathbf{3}^{\cdot-}$ and $\mathbf{5}^{\cdot-}$–$\mathbf{8}^{\cdot-}$; they were confirmed, in part, by specific deuterations (see above). The drastic decrease in the $|a_H|$ values of the *ortho*- and *para*-protons in $\mathbf{12}^{\cdot-}$ relative to those in the remaining radical anions will be addressed in the *Discussion*. Finally, the coupling constants of protons in the radical anion of (*E*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene (**13**), a di-*tert*-butyl substituted (*E*)-stilbene, were assigned by comparison with those for $\mathbf{1}^{\cdot-}$.

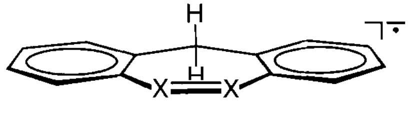
Discussion. – In the following, frequent use will be made of optimized molecular geometries derived from theoretical calculations by the semi-empirical MNDO [17] and AM1 [18] procedures. This information is particularly valuable for radical anions, of which structural data are generally not available by experimental methods such as X-ray crystallography and/or electron diffraction. For $\mathbf{13}^{\cdot-}$ and $\mathbf{14}^{\cdot-}$, the calculations were, to a large extent, carried out by another research group, and they will be reported in more detail elsewhere [19].

Stilbene Series. A striking feature of the two isomeric stilbene radical anions $\mathbf{1}^{\cdot -}$ and $\mathbf{3}^{\cdot -}$ (*Table 1*) is the near-equality of the coupling constants of their Ph protons. The π-spin distribution thus appears to be only marginally altered by the increased deviation from planarity in the (Z)-configurated radical anion $\mathbf{3}^{\cdot -}$ relative to its (E)-isomer $\mathbf{1}^{\cdot -}$. As the benzene rings remain essentially planar, the steric hindrance must be relieved by rotating the Ph groups out of coplanarity with the central C=C bond and/or by twisting about this bond. Electron-diffraction studies of **3** [20] and theoretical calculations for **3** and $\mathbf{3}^{\cdot -}$ indicate that the problem of the steric hindrance is met in both ways. Whereas, in the neutral molecule, it is relieved mainly by rotating the Ph groups, twist about the central bond becomes more effective in the radical anion. This twist should be responsible for the decrease in the absolute value $|a_H|$ of the α-protons attached to the bond in question, as a_H is −0.449 mT for $\mathbf{1}^{\cdot -}$ but −0.268 mT for $\mathbf{3}^{\cdot -}$. The decrease is caused by positive contributions to a_H arising from π,σ-spin delocalization, which partially compensate the negative ones due to π,σ-spin polarization governing the coupling constants of the α-protons in planar π-radicals [21].

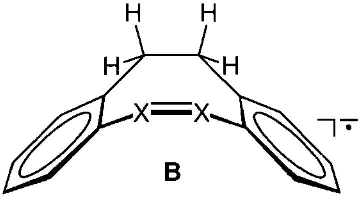
The coupling constants of the Ph protons in $\mathbf{3}^{\cdot -}$ can be compared with the analogous values for the radical anions $\mathbf{5}^{\cdot -}$–$\mathbf{9}^{\cdot -}$ and $\mathbf{11}^{\cdot -}$ also containing the (Z)-stilbene π-system. The four 1,2-diphenylcycloalkene radical anions, $\mathbf{5}^{\cdot -}$–$\mathbf{8}^{\cdot -}$, represent a sequence, in which the steric hindrance of the Ph substituents increases with the growing size of the cycloalkene ring. The steady decrease in the absolute value $|a_H|$ of the *para*-proton in the order $\mathbf{5}^{\cdot -}$ (−0.458 mT), $\mathbf{6}^{\cdot -}$ (−0.424 mT), $\mathbf{7}^{\cdot -}$ (−0.381 mT), and $\mathbf{8}^{\cdot -}$ (−0.359 mT) may reflect a slight shift of the π-spin population from the Ph groups to the central C=C bond. Noteworthy is the near-equality of this a_H value for $\mathbf{7}^{\cdot -}$ and that of the *para*-proton in $\mathbf{3}^{\cdot -}$ (−0.386 mT), which suggests a similar π-spin distribution. Theoretical calculations attest comparable deviations from planarity in the two radical anions, while such deviations should be less pronounced in $\mathbf{5}^{\cdot -}$ and $\mathbf{6}^{\cdot -}$ and more in $\mathbf{8}^{\cdot -}$. Effect of twisting about the central bond in $\mathbf{5}^{\cdot -}$–$\mathbf{8}^{\cdot -}$ cannot, however, be verified experimentally, because the C-atoms of that bond do not bear protons. On the other hand, such α-protons are present in $\mathbf{9}^{\cdot -}$ and $\mathbf{11}^{\cdot -}$, and their coupling constants (−0.422 and −0.428 mT, resp.) resemble the corresponding value for the (E)-configurated $\mathbf{1}^{\cdot -}$ (−0.449 mT) rather than that for $\mathbf{3}^{\cdot -}$ (−0.268 mT), thus pointing to a greatly reduced twisting about the central C=C bond. The changes in the coupling constants of the *para*-protons on passing from $\mathbf{9}^{\cdot -}$ (−0.422 mT) to $\mathbf{11}^{\cdot -}$ (−0.387 mT) are relatively small, being almost the same as those found on going from $\mathbf{6}^{\cdot -}$ to $\mathbf{7}^{\cdot -}$. According to theoretical calculations, $\mathbf{9}^{\cdot -}$ should be almost planar, while for $\mathbf{11}^{\cdot -}$, two geometric forms must be considered, the 'twisted' and the tub one (**A** and **B**, resp., in *Fig. 4*). The twisted form, in which the benzene rings are only slightly rotated out of coplanarity with the central C=C bond, is predicted to be more stable than its tub counterpart (energy difference: 26 and 38 kJ mol^{-1} by MNDO and AM1, resp.).

The by far highest deviations of the π-system from planarity in the stilbene series considered here are found in **13** and **14**, substituted by the bulky *tert*-butyl groups at the central C=C bond. The X-ray crystallographic structure analyses of **13** [22] and **14** [23] revealed that this bond is not twisted but that the Ph groups are perpendicular to its plane. For the dianions $\mathbf{13}^{2-}$ and $\mathbf{14}^{2-}$, AM1 calculations predict a twist by 90° about the central bond which thus largely losses its C=C bond character [19]. The potential





9 X = CH
10 X = N



11 X = CH
12 X = N

Fig. 4. *Geometries of* $\mathbf{9}^{\cdot-}$*–*$\mathbf{12}^{\cdot-}$ *as calculated by MNDO and AM1.* The 'twisted' structure **A** (symmetry C_2) of $\mathbf{11}^{\cdot-}$ and $\mathbf{12}^{\cdot-}$ is predicted to be lower in energy than the tub-shaped one **B** (C_s).

hypersurface has only one energy minimum, so that $\mathbf{13}^{2-}$ and $\mathbf{14}^{2-}$ cannot be distinguished, and the common dianion consists, in principle, of two mutually orthogonal benzyl anions. The structures of the radical anions $\mathbf{13}^{\cdot-}$ and $\mathbf{14}^{\cdot-}$ are predicted to be intermediate between those of the neutral molecules and the dianion, with the potential hypersurface being rather flat about the C_{ipso}–C=C–C_{ipso} central fragment [19]. The two energy minima, separated by a low barrier, represent two configurations, of which one is closer to (*E*) ($\mathbf{13}^{\cdot-}$) and the other to (*Z*) ($\mathbf{14}^{\cdot-}$); the former configuration has a minimum slightly deeper than the latter. The disproportionation reaction of the radical anions, $2 \times \mathbf{13}^{\cdot-}(\mathbf{14}^{\cdot-}) \rightarrow \mathbf{13}(\mathbf{14}) + \mathbf{13}^{2-}(\mathbf{14}^{2-})$, should be greatly favored over the analogous reaction, $2 \times \mathbf{1}^{\cdot-}(\mathbf{3}^{\cdot-}) \rightarrow \mathbf{1}(\mathbf{3}) + \mathbf{1}^{2-}(\mathbf{3}^{2-})$, for the parent stilbenes, in line with the observed facile reduction of **13** and **14** directly to the dianion(s).

The protons in the Ph groups in $\mathbf{13}^{\cdot-}$ have coupling constants which are comparable to those for the parent $\mathbf{1}^{\cdot-}$. Admittedly, the $|a_H|$ value of the *para*-proton coupling constant for $\mathbf{13}^{\cdot-}$ (–0.338 mT) is markedly smaller than for $\mathbf{1}^{\cdot-}$ (–0.398 mT), being the lowest one in the stilbene series, but it is still within the range appropriate for such protons. Thus, a redistribution of the π-spin population between the benzene rings and the central bond must, even in this case, be only limited. It is noteworthy that the $|a_H|$ value (0.085 mT) of the *tert*-butyl protons is unusually large for γ-protons[2]. Coupling constants calculated by the method of *d*ensity *f*unction *t*heory (DFT) for the AM1-optimized geometry of $\mathbf{13}^{\cdot-}$ [19] are in overall agreement with their observed counterparts[3].

Azobenzene Series. The hyperfine data in this series are restricted to the radical anion of (*E*)-azobenzene (**2**) and of the two tricyclic derivatives **10** and **12** of (*Z*)-azobenzene (*Table 2*). The similar coupling constants of the α-protons in the corresponding positions of $\mathbf{2}^{\cdot-}$ and $\mathbf{10}^{\cdot-}$, particularly those of the *para*-protons ($\mathbf{2}^{\cdot-}$: –0.320 mT; $\mathbf{10}^{\cdot-}$: –0.305 mT), indicate that the π-spin distribution in the two radical anions does not greatly differ. Thus, the marked increase in the a_N values on going from $\mathbf{2}^{\cdot-}$ (+0.478 mT) to $\mathbf{10}^{\cdot-}$

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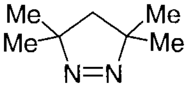
[3] Assignments of the a_H values made in *Table 1* for $\mathbf{13}^{\cdot-}$ is supported by these calculations, with the exception of the two *meta*-positions; the protons in the *m*-positions are predicted to have slightly larger coupling than those in the *m'*-positions.

(+0.644 mT) can rather be attributed to some p,s-rehybridization of the N-atoms [24] than to a substantial shift in the π-spin population to the azo group.

Striking changes in most hyperfine data occur in passing from $\mathbf{2}^{\cdot-}$ and $\mathbf{10}^{\cdot-}$ to $\mathbf{12}^{\cdot-}$. The absolute values of the negative coupling constants of the *para*- and *ortho*-protons are drastically lowered ($\mathbf{10}^{\cdot-}$: −0.305 and −0.234 mT; $\mathbf{12}^{\cdot-}$: −0.108 and −0.096 mT), while the positive a_H values of the *meta*-protons are less affected ($\mathbf{10}^{\cdot-}$: +0.132 and +0.083 mT; $\mathbf{12}^{\cdot-}$: +0.073 and +0.063 mT). Moreover, the remarkable increase in the coupling constant of the ^{14}N nuclei in $\mathbf{12}^{\cdot-}$ relative to the a_N values for $\mathbf{2}^{\cdot-}$ and $\mathbf{10}^{\cdot-}$ can hardly be brought about by p,s-rehybridization alone. This ^{14}N-coupling constant (+0.915 mT) resembles those for the radical anions of cyclic (*Z*)-azoalkanes ($\mathbf{15}^{\cdot-}$: +0.918 mT; $\mathbf{16}^{\cdot-}$: +0.871 mT; $\mathbf{17}^{\cdot-}$: +0.878 mT) [16], in which the π-spin population is essentially confined to the azo group.



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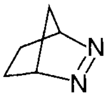

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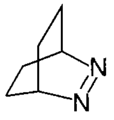

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Theoretical calculations predict similar geometries for the two pairs of isoelectronic radical anions, $\mathbf{9}^{\cdot-}$ and $\mathbf{10}^{\cdot-}$ on the one hand and $\mathbf{11}^{\cdot-}$ and $\mathbf{12}^{\cdot-}$ on the other (*Fig. 4*). Thus, $\mathbf{10}^{\cdot-}$ should, like $\mathbf{9}^{\cdot-}$, be essentially planar, while for $\mathbf{12}^{\cdot-}$, as for $\mathbf{11}^{\cdot-}$, the 'twisted' and the tub form must be taken into account. Again the twisted form **A** is predicted to be more stable than the tub form **B**, albeit less distinctly (energy difference: 6 and 28 kJ mol^{-1} by MNDO and AM1, resp.). The striking changes in the hyperfine data on passing from $\mathbf{10}^{\cdot-}$ to $\mathbf{12}^{\cdot-}$, as contrasted with the moderate ones on going from $\mathbf{9}^{\cdot-}$ to $\mathbf{11}^{\cdot-}$, would, therefore, be difficult to rationalize if both $\mathbf{11}^{\cdot-}$ and $\mathbf{12}^{\cdot-}$ existed in the same twisted form. This is because the coupling constants observed for $\mathbf{12}^{\cdot-}$ are characteristic of π-radicals in which the benzene moieties are strongly tilted out of coplanarity with the π-system bearing the bulk of the spin population (tilt angle > 50°) [25]. Such a tilt is predicted for the benzene rings in the tub forms of $\mathbf{11}^{\cdot-}$ and $\mathbf{12}^{\cdot-}$ (*Fig. 4*) but not in their twisted counterparts. Thus, the hyperfine data for $\mathbf{12}^{\cdot-}$ strongly suggest that, unlike $\mathbf{11}^{\cdot-}$ and at some variance with the results of theoretical calculations, this radical anion prefers the tub over the twisted form. The driving force for such a preference must be the tendency to shift the charge and spin populations from the benzene rings to the electronegative azo group.

Conclusions. – With the notable exception of the a_H value at the central C=C bond in $\mathbf{3}^{\cdot-}$, deviations of the stilbene π-system from planarity have only a moderate effect on the coupling constants of the α-protons in the nine radical anions $\mathbf{1}^{\cdot-}$, $\mathbf{3}^{\cdot-}$, $\mathbf{5}^{\cdot-}$–$\mathbf{9}^{\cdot-}$, $\mathbf{11}^{\cdot-}$, and $\mathbf{13}^{\cdot-}$. Although the corresponding radical anions in the azobenzene series are restricted to $\mathbf{2}^{\cdot-}$, $\mathbf{10}^{\cdot-}$, and $\mathbf{12}^{\cdot-}$, it is evident that the above statement does not hold for $\mathbf{12}^{\cdot-}$. The hyperfine data for this radical anion, which strongly differ from those for $\mathbf{2}^{\cdot-}$ and $\mathbf{10}^{\cdot-}$, point to a substantial shift of the π-spin population from the benzene rings to the azo group, as a consequence of the hindered coplanarity of the constituent π-moieties. As stated in the *Introduction*, such a shift is not unexpected, considering the electron affinities of these moieties. Whereas ethene has an electron affinity even lower than that of benzene [26], the azo group is a fairly good electron acceptor favorable for the accomodation of the negative charge in radical anions.

Experimental. – The compounds **9**–**12** were prepared according to procedures reported in the literature: **9** [14] [27], **10** [28], **11** [29], **12** [30]. In the synthesis of D_2-**10**, $LiAlD_4$ replaced $LiAlH_4$ for the conversion of 2,2′-dinitrophenone into the final product. 2,2′-Dinitrophenone was prepared by oxidation of 2,2′-dinitrodiphenylmethane which was obtained from 4,4′-diaminodiphenylmethane by nitration and subsequent deamination, using generally known procedures [31]. D_2-**12** was synthesized starting with 4-bromo-2-nitrotoluene prepared by the *Sandmeyer* reaction from the corresponding amine. Condensation of this nitrotoluene yielded 1,2-(4-bromo-2-nitrophenyl)ethane [32] which was converted with $LiAlD_4$ to D_2-**12**. The syntheses of **13** [33] and **14** [34] were described previously.

The ESR spectra were taken on *Varian-E9* and *-E3* instruments, while a *Bruker-ESP-300* system served for ENDOR and TRIPLE-resonance studies. The Hg/Xe lamp for UV irradiation was a 1000-W apparatus of *PTI*, Hamburg.

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